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(54) MOULDING THERMOPLASTIC ARTICLES

(71) We, INVENTA A.G., FUR FORSCHUNG UND PATENTVERWERTUNG, Zurich, a Swiss Body Corporate, residing at Stampfenbachstrasse 38, Zurich, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is well known now to make seamless hollow bodies, for example large storage tanks for liquids, by rotary moulding. They are usually formed from thermoplastic polymeric material introduced into the mould in powder form, common materials being polyethylene and soft polyvinyl chloride. However there materials do not render the bodies sufficiently strong for some purposes. The use of polyamides would give better strength and better resistance to certain liquids, for example oil and petrol, but is generally impossible, partly due to the higher cost of polyamide powders.

It might be thought possible to form the polyamide in situ in the mould by anionic polymerisation of lactam, i.e. by polymerisation of anhydrous lactam in the presence of an alkaline catalyst and suitable activator, generally in conventional manner. However it is difficult to handle and meter into the mould the exact amounts of lactum and activator that are required and it is generally found that unsatisfactory results are obtained. One difficulty is that the storage stability of the necessary mixture of lactam and activator is rather poor. Another difficulty is that due to variations in atmospheric moisture and atmospheric oxygen it is difficult to obtain reproducable polymerisation results and in some instances, when there is a high atmospheric moisture content, polymerisation may be prevented completely.

A further, very important, difficulty arises from the fact that the mixture is usually heated for polymerisation to a temperature of 130 to 160°C but some polymerisation, to form an oligomer, occurs at a much lower temperature, for example about 90°C. At such low tempeartures the oligomer is precipitated out from the melt and cannot undergo further polymerisation. As a result the article formed often has a white surface and the polymer has low relative viscosity and inadequate mechanical properties for many purposes.

According to the invention a moulded body of polyamide is produced by feeding into a mould a mixture of lactam and activator for anionic polymerisation of the lactam and heating the mixture to melt and polymerise the lactam and form the polyamide while rotating the mould, in which process the activator is enclosed within film packs from which it is released for activating the polymerisation only at temperatures below the polymerisation temperature such that the oligomers formed on release can dissolve into the lactam melt. As a result it is not necessary to use the very costly apparatus that has previously been required for melting the mix and metering the components and in fact the process for making polyamide articles can be conducted almost as simply as the conventional rotary moulding process for making polyethylene articles. By the process hollow articles having the strength expected of polyamide articles may be obtained.

As lactam there can be used any suitable polymerisable lactam or lactam mixture. Typical lactams include caprolactam and laurolactam. Advantageously a mixture of such lactams may be used, for example mixture containing caprolactam and laurolactam in proportions between 95:5 and 80:20 may be used, such mixtures being particularly desirable for economic reasons.

The activator consists of one or more ingredients that activate the polymerisation of the lactam on heating, with the result that until a desired temperature is reached and the activator is released from the packs polymeriastion is substantially prevented. The activator may comprise any known activator for anionic polymerisation of lactams. Thus generally the activator will comprise an alkali compound, to serve as the catalyst, and

will usually comprise also one or more accelerators or cocatalysts.

Suitable alkali compounds include Na and NaH. They may be used in pure form or suspended in inert carriers and/or mixed with lactam.

Suitable accelerators or cocatalysts include, for example, acetyl lactams, isocyanates and polycarbodiimides or mixtures thereof. They may be used in pure form or mixed with lactams or inert carriers.

When the activator comprises more than one ingredient the ingredients may be packed separately or as mixtures. The packs may be formed by known methods to any desired size. The packs may be heat sealed packs. The films of the packs preferably melt on heating to the desired temperature to release the activator, or may dissolve in the lactam at the desired temperature. Preferably the film is a material which melts and dissolves in the lactam at the desired temperature. Thus the film should be both soluble and compatible in the hot reaction mixture and also in the resultant polymer. Suitable film materials are polyamides, preferably polyamide 11 or polyamide 12. Such films have the advantage of giving excellent protection against atmospheric effects. Storage tests have shown that catalysts and cocatalysts heat-sealed in films of polyamide 12 show no loss of activity after three months. Other suitable film materials include polyethylene and polypropylene.

The process of the invention is conducted by feeding a mixture of lactam and activator, enclosed within film packs, to a suitable mould or by feeding them separately and mixing them in the mould. The lactam may be introduced in solid or liquid form. The mould is rotated and heated to the desired polymerisation temperature. The polymerisation temperature should be below the melting temperature of the polyamide, so as to prevent the formation of cavities, and the optimum is generally from 130 to 200°C. The film within which the activator is enclosed should be material that releases the activator at temperatures only slightly below the polymerisation temperature. Thus generally it will only release the activator at temperatures above 100°C and preferably only at temperatures of more than 125°C, especially when the polymerisation temperature is 130 to 160°C. The criterion is that the film should only release the activator at temperatures below the optimum polymerisation temperature can dissolve into the lactam melt.

The following are some examples, Examples 1, 3 and 4 being of the invention while Example 2 is a comparative Example.

EXAMPLE 1

1.5 kg of caprolactam are fed at room temperature into a simple, two part, cylindrical rotary hollow mould of 2 mm aluminium sheet with a volume of 20 litres. 3 g of sodium hydride suspension (50% NaH in paraffin oil) mixed with about 15 g of caprolactam and heat-sealed in polyamide 12 film 100 μ thick, and 13 g of a mixture consisting of 56 parts by weight of acetyl lactam, 24 parts by weight of palycarbodiimide and 2 parts by weight of caprolactam, heat-sealed in polyamide 12 film 100 μ thick, are thereupon added to the pulverulent caprolactam in the mould.

The mould is closed and rotated for 10 minutes in an oven at 160 to 170°C. The finished part is thereafter removed from the mould while still hot.

This is found to be satisfactory casting with a good inner and outer surface and very good mechanical properties due to good, even polymerisation. The polymer has a relative viscosity of 5.5—6 in H_2SO_4. The extract in water is 3%.

EXAMPLE 2

Into the same mould as used in Example 1 there are again fed 1.5 kg of caprolactam, with which, however, the amounts of catalyst and cocatalyst given in Example 1 have been mixed directly without packing them separately. The mould is closed and rotated under the same conditions as in Example 1. After the mould has been opened, it is found that very incomplete polymerisation has occurred. The finished part obtained is covered with a thick white layer of monomers and oligomers.

EXAMPLE 3

9 kg of caprolactam and 1 kg of laurolactam are fed into the mould for a round container or tank with a capacity of about 150 litres. 5 packs each consisting of 4 g of sodium hydride suspension (50% NaH in paraffin oil) mixed with 15 g of caprolactam in polyamide 12 film and 5 packs each consisting of the cocatalyst mixture in polyamide 12 film as in Example 1 are added thetreto. A pack of catalyst or cocatalyst mixture is sufficient in each case for 2 kg of lactam mixture and is heat-sealed in 100 μ film of polyamide 12. The mould is closed and rotated for 15 minutes in an oven at 180 to 190°C.

The finished container may be removed from the mould in the hot state. It has a faultless surface. The polymer has a relatively viscosity of 6 in sulphuric acid. The extract in water is less than 3%.

EXAMPLE 4

The process is performed under the same conditions as in Example 1. The catalyst and cocatalyst are not heat-sealed in poly-

amide film, however, but i[illegible]0 μ polyethylene film.

The polymerisation proceeds likewise in a satisfactory manner. Remains of the melted film are distributed and embedded in the container wall.

WHAT WE CLAIM IS:—

1. A process in which a moulded body of polyamide is produced by feeding into a mould lactam and activator for anionic polymerisation of the lactam and heating the mixture of lactam and activator to melt and polymerise the lactam and form the polyamide while rotating the mould, in which process the activator is enclosed within film packs from which it is released for activating the polymerisation only at temperatures below the polymerisation temperature such that the oligomers formed on release can dissolve into the lactam melt.

2. A process according to claim 1 in which the film of the packs is such that the activator is released from the packs at a temperature above 100°C.

3. A process according [illegible]claim 2 in which the temperature at whi[illegible]the activator is redleased is above 125°C.

4. A process according to any preceding claim in which the film of the packs is formed of polyamide 11 or polyamide 12.

5. A process according to any preceding claim in which the lactam is caprolactam.

6. A process according to any of claims 1 to 4 in which the lactam is laurolactam.

7. A process according to any preceding claim in which the lactam is a mixture of 5 to 20% laurolactam with 80 to 95% caprolactam.

8. A process according to claim 1 substantially as herein described with reference to Examples 1, 3 or 4.

9. A moulded body made by a process according to any preceding claim.

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